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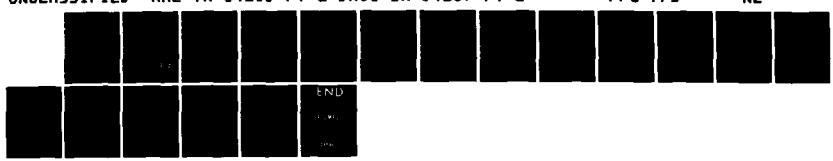

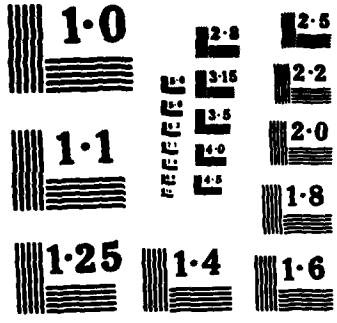

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CALCULATION OF THE GLASS TRANSITION TEMPERATURES OF LINEAR POLYMERS

PART 1- RULES FOR HIERARCHICAL ORDERING OF THE DATA SET

by

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SUMMARY

The rational ordering of polymers in a large data set for the correlation of glass transition temperature (Tg) with structure requires the establishment of seniority criteria. An extension of polymer nomenclature rules published by the International Union of Pure and Applied Chemistry is proposed and applied, with examples, to the groups in a large polymer data set. The rules can be extended to cover new polymers without upsetting the original order.

Departmental Reference: Materials/Structures 108

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1 INTRODUCTION

In a recent memorandum[1] the importance and significance of the transition temperatures of polymers was described and earlier papers concerned with the calculation of the glass transition temperature (Tg) were listed. Many reasons were given to justify the Tg as one of the most important properties of a polymer especially in the sense that the practical role of a polymer depends to a great extent on the Tg value. With that in mind it is not surprising that the estimation of Tg in advance of synthesis has been a prime goal for many of the workers engaged in the synthesis, or development, of new useful polymers.

For the estimation of Tg, which is determined by the segmental relaxation rate of the constituent groups in polymers, it is highly desirable to base empirical calculations on as large a date set as practicable. It is hoped thereby to enhance the reliability of the data and, by increasing the number of different polymer environments in which constituent groups are represented, to increase confidence in the prediction of Tg values of polymers outside the data set. The data set in the series of calculations to be described comprises over 1100 polymers and is the largest set so far used in this type of work. In order to avoid duplication of structures in this set and to enable any particular polymer to be located as easily as possible, the set must be ordered. Thus, a set of criteria must be established which distinguishes between the structural characteristics of every polymer present. It is the object of this Report to define the criteria which have been employed.

2 SENIORITY CRITERIA FOR CONSTITUENT GROUPS

The seniority criteria for groups in polymers are based on rules described in an earlier report[2] with some enhancement and amendment. Thus; diradical seniority is basically determined according to the IUPAC tentative rules for systematic polymer nomenclature[3]. All the information necessary to extend the system is presented in this Report.

2.1 Criteria for all categories of groups

Polymer groups are divided into main-chain (MC) groups, which are most senior, and side-chain (SC) groups: amongst SC groups, a monoradical (terminal) group is subordinate to any multi-radical group. Each of these three categories are sub-divided into four further categories which, in decreasing order of seniority are:

I containing a heterocyclic ring;

II containing an element other than C (hydrogen being regarded as a substituent);

III containing a carbocyclic ring;

IV containing a carbon chain acyclic group.

Numbered criteria for determining seniorities within these classes are provided in three sets appropriate to categories I, II, III and IV. All the criteria could be combined into one system, but it is easier in practice to make the above subdivisions first and apply special criteria to the individual sets. A group which satisfies the criteria corresponding to the lowest criterion number has the highest seniority.

In the application of the criteria to SC groups which have branches, the SC groups are given the status of MC groups and the branch groups are regarded as side-chains to these "promoted" MC groups.

In the rules which follow, heteroatoms which are not actually in a ring, but are bonded to rings, are regarded as substituents, eg oxo substituents. When heteroatoms are bonded to acyclic structures they are also regarded as substituents to these structures, eg O bonded to S, or C is a substituent to the group containing S or C. Rings are numbered according to The Ring Index and otherwise according to IUPAC Nomenclature rules In ring systems, it is assumed that groups and their mirror images have the same numbering.

2.2 Criteria for heterocyclic groups (categories I MC and I SC)

(a) Containing nitrogen and a heteroatom other than nitrogen as high as possible in the descending order, O, S, Se, Te, P, As, Sb, Bi, Si, Ge, Sn, Pb, B, and Hg, the positions of other atoms being determined within this order by their positions in the periodic table.

(b) Containing nitrogen.

(c) Containing a heteroatom other than nitrogen as high as possible in the descending order, O, S, Se, Te, P, As, Sb, Bi, Si, Ge, Sn, Pb, B, and Hg: the positions of other atoms are determined within this order by their positions in the periodic table.

(d) Having the largest number of rings which are fused (joined at more than one atom).

(e) Having the largest number of the largest rings.

(f) Having the largest number of heteroatoms (excluding substituents like F, oxo etc as noted above).

(g) Having the greatest variety of heteroatoms.

(h) Having the largest number of heteroatoms highest in the order of criterion(1).

(j) Having the most unsaturated system (largest number of multiple bonds).

(k) Having the lowest numbers for points of attachment between rings within the assembly consistent with the fixed numbering of the parent ring.

(l) Having the lowest heteroatom locants.

(m) Having the largest number of free (radical) bonds.

(n) Having the largest number of heteroatom substituents.

(o) Having the lowest MC free-bond locants.

(p) Having the lowest SC free-bond locants.

(q) Having the lowest substituent locants.

(r) Having substituents whose names are highest in alphabetical order.

(s) Having a cis configuration.

(t) Having a trans configuration.

(u) Having a specification other than cis or trans.

2.3 Criteria for carbocyclic groups (categories III MC and III SC)

(a) Having the largest number of rings which are fused (joined at more than one atom).

(b) Having the largest number of the largest rings.

(c) Having the largest number of atoms common to rings.

(d) Having the most unsaturated system (largest number of multiple bonds).

(e) Having the largest number of free bonds.

(f) Having the lowest locant numbers at the first point of difference for ring junctions.

(g) Having the largest number of heteroatom substituents.

(h) Having the lowest MC free-bond locants.

(j) Having the lowest SC free-bond locants.

(k) Having the lowest substituent locants.

(l) Having substituents whose names are highest in alphabetical order.

(m) Having a cis configuration

(n) Having a trans configuration.

(o) Having a specification other than cis or trans.

2.4 Criteria for acyclic groups (categories II MC, II SC, and IV SC)

(a) Containing a heteroatom as high as possible in the descending order F, Cl, Br, I, O, S, Se, Te, N, P, As, Sb, Bi, Si, Ge, Sn, Pb, B and Hg: the positions of other atoms being determined within this order by their positions in the periodic table.

(b) Having the largest number of heteroatoms.

(c) Having the greatest variety of heteroatoms.

(d) Having the largest number of heteroatoms highest in the order of criterion (a).

(e) Having the largest number of MC multiple bonds.

(f) Having the largest number of multiple bonds between MC and SC or substituents.

(g) Having the lowest heteroatom locants.

(h) Having the largest number of free bonds.

(j) Having a heteroatom substituent highest in the order of criterion (a).

(k) Having the largest number of heteroatom substituents.

(l) Having the greatest variety of heteroatom substituents.

(m) Having the largest number of heteroatom substituents highest in the order of criterion (a).

(n) Having the lowest MC free-bond locants.

(o) Having the lowest SC free-bond locants.

(p) Having a cis configuration.

(q) Having a trans configuration.

(r) Having an isotactic configuration.

(s) Having a syndiotactic configuration.

(t) Having a specification other than cis, trans, isotactic or syndiotactic.

The application of these seniority rules to the polymers in the present data set leads to the set of groups which are arranged in hierarchical order in Table 1. Within the calculations themselves, groups with fluorine substituents have been treated as though a fluorine substituents were part of the group to which it was attached rather than a separate group. Such combined groups have been included in Table 1 for the purpose of keeping all the group drawings together, but they have been given the same seniority as they would have had if the fluorine substituents were replaced by free bonds. Each group has been given an arbitrary number for reference purposes. It will be noticed that both asymmetric groups and their mirror images are shown, for example, the second and third groups denoted 170 and 167. These groups are, of course, identical and have the same seniority, but it is necessary to use both forms in order to discriminate between different points of attachment to them. This will be made clear in the numerical analysis of polymers which is described in a later report in this series. Main- and side-chain groups which belong to series of identical groups of general formula $-(CX)_n-$ have all been distinguished by different numbers for different values of n. In any particular series they have the same seniority, but in polymer situations, the rules for ordering polymers place the sequences in the order shown. This becomes apparent in detailed analysis studies. The drawings were plotted from a computer file of data used for drawing polymer structures in which some structures have lengthened bonds to avoid overlapping structures. For this reasons some of the bonds on some drawings are shown to be longer than would be expected. All groups up to and including group 321 on page 5 of Table 1 are MC groups and all groups thereafter are SC groups, all groups after group 7 on page 6 are terminal SC groups. MC bonds are shown as horizontal lines up to group 321, bonds at any other angle denote SC attachments.

3 SENIORITY CRITERIA FOR POLYMERS

The following rules are in priority order. The most senior polymer is that containing in the chemical repeating unit (CRU) the:-

(1) Most senior group (see seniority rules for atoms and groups) which is placed at the extreme left hand end of a graphical representation.

(2) Shortest bridge (number of atoms in the MC) from the first group (the most senior) to the next occurrence of this group in the infinite polymer (not in the CRU, which may contain only one such group). The shortest bridge is placed at the extreme left hand end of the graphical representation.

(3) Shortest sequence of bridges in the infinite polymer between the most senior group and the next occurrences of groups which are identical with the most senior group. A bridge sequence of 1,1,4,9 is senior to a bridge sequence of 1,3,1,5. (At the first point of difference 1,1,4,9 has the shortest bridge.) Note, therefore, that the most senior bridge is not necessarily that with the most senior group in it.

(4) Most senior group at the first point of difference proceeding from left to right through the CRU regardless of the seniority of the groups which occur in the bridge(s) beyond the first point of difference.

(5) Most senior SC, which is that with the most senior group in the first SC from the left, at the first point of difference travelling away from the MC and proceeding if necessary, down any branch. If, in two polymers being compared, the first SC from the left are identical, the second then the third, etc, SC are compared until the first point of difference is reached.

(Asymmetrical groups and their mirror images are regarded as having the same seniority.)

Table 2 has been constructed to illustrate the application of the seniority criteria described in this section. The polymers are in decreasing seniority order from left to right and from top to bottom. Rule 1 applies to all polymers. Rule 2 places Polymer 849 senior to Polymer 271 because in the former the first bridge between the first group (-O-) and the next occurrence of this group consists of a $-CH_2-$ group whereas the comparative bridge in Polymer 271 comprises two groups (-CO-CO-) which is longer. Rule 3 places Polymer 1157 senior to Polymer 1162 because although a *m*-phenylene group is senior to a $-CF_2-$ group, the sequence of bridges in the respective polymers is 3, 9 and 3, 12 which makes the former sequence senior. Rule 4 places Polymer 1250 senior to Polymer 1248 because the polymers have the same bridge sequence, that is 0, 15 and at the first point of difference from the left the group -O- is senior to the group -NH. Rule 5 places the next four polymers in the order 27, 34, 29, 15. Polymer 27 is senior to Polymer 34 because in the SC the second group in the horizontal branch from the first branch point is senior to its comparable group in Polymer 34 at the same atom-distance from the MC. ($-CH-$ is senior to $-CH_3$ and also $-CH_2-$ is senior to $-CH_3$ in the vertical branch.) Polymer 34 is senior to Polymer 29 because the nearest group to the horizontal SC branch point ($-CH_2-$) is senior to the group ($-CH_3$) in the corresponding position in Polymer 29. Polymer 29 is senior to Polymer 15 because at the first point of difference, which occurs at the second branch point in the SC of Polymer 29, the group $-\dot{C}H-$ is senior to $-CH_2-$) which is the corresponding group in Polymer 15.

4 CONCLUSIONS

A system is proposed for the unambiguous classification of single-strand organic polymers in hierarchical order. The system greatly facilitates the location of polymers within classified lists and eliminates the need for multiple naming and indexing: it is therefore particularly appropriate for polymer data handbooks and like publications. The system can readily be extended by the application of rules of nomenclature in current use, without upsetting the existing order.

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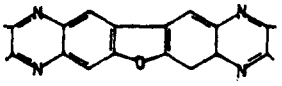
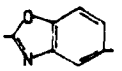
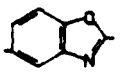
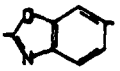
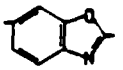
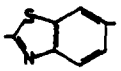
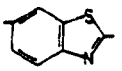
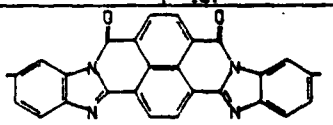
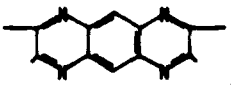
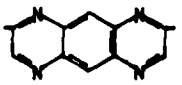
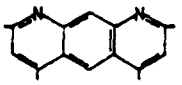
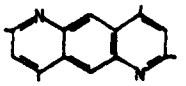
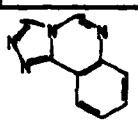
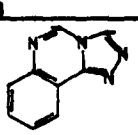
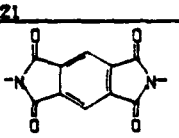
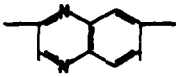
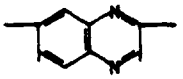
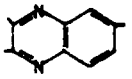
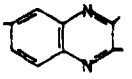
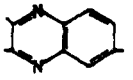
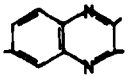
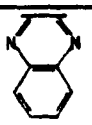
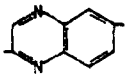
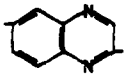
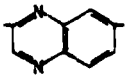
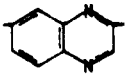
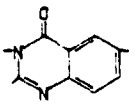
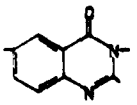
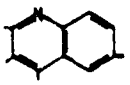
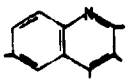
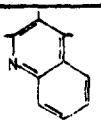
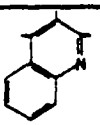
GROUPS IN HIERARCHY ORDER

 175		 170	 167
 179	 87	 93	 188
 181	 195	 86	 197
 198	 208	 228	
 209	 209	 221	 220
 229	 230	 234	 241
 242	 239	 240	 235
 236	 244	 237	 238
 245	 246	 232	 233
 248	 249	 252	 253

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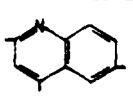
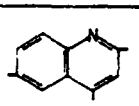
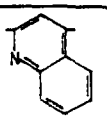
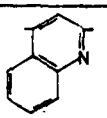
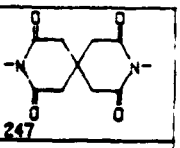
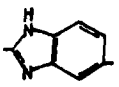
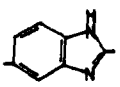
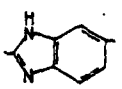
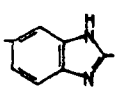
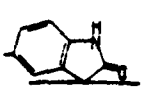
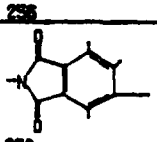
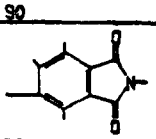
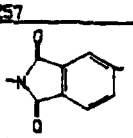
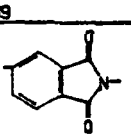
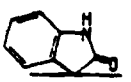
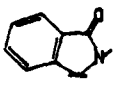
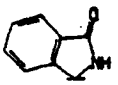
 250	 251	 254	 255	 247
 256	 90	 257	 89	 226
 260	 261	 243	 84	 80
 82	 81	 286	 265	 287
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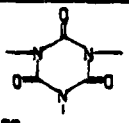
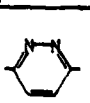
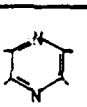
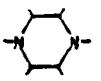
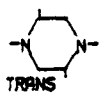
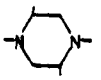
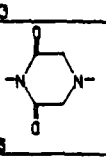
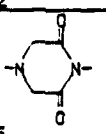
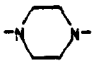
 289	 99	 143	 202	 278
 205	 270	 276	 275	 72
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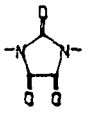
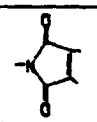
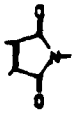
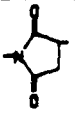
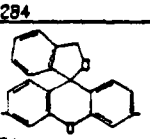
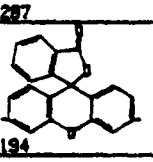
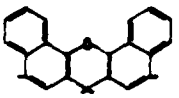
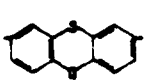
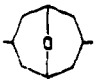
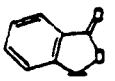
 271	 272	 285	 284	 287
 286	 288	 282	 94	 194
 3	 298	 4	 277	 83
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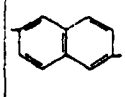
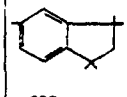
 65	 222	 69	 186	 154	 199	 224	 58
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 47	 49	 51	 189	 166	 41	 40	 39
 38	 37	 CIS 8	 TRANS 9	 34	 184	 183	 43
 TRANS 42	 -C≡C- 29	 28	 191	 CIS 35	 TRANS 150	 176	 CIS 148
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136	132	402	403	404	405	406	407
408	409	410	411	412	413	414	415
416	417	418	419	420	421	ISOTACTIC -CH- 18	SYNDIOTACTIC -CH- 17
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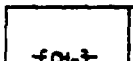
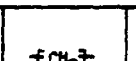
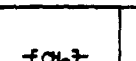
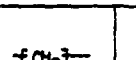
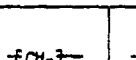
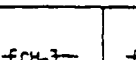
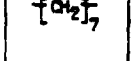
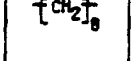
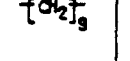
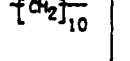
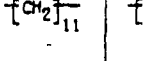
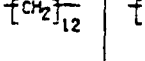
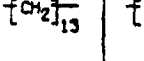
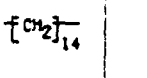
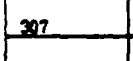
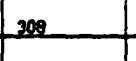
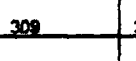
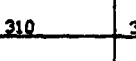
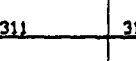
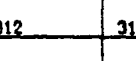
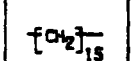
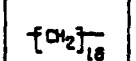
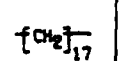
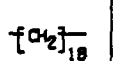
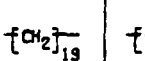
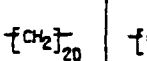
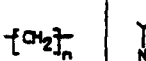
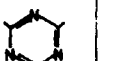
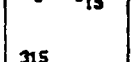
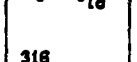
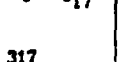
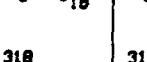
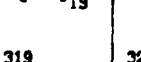
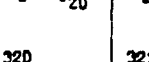
Table 1 (Continued)

 307	 309	 309	 310	 311	 312	 313	 314
 315	 316	 317	 318	 319	 320	 321	 210
 207	 158	 108	 211	 119	 117	 218	 105
 103	 114	 213	 171	 214	 173	 122	 135
 70	 60	 187	 142	 58	 57	 54	 161
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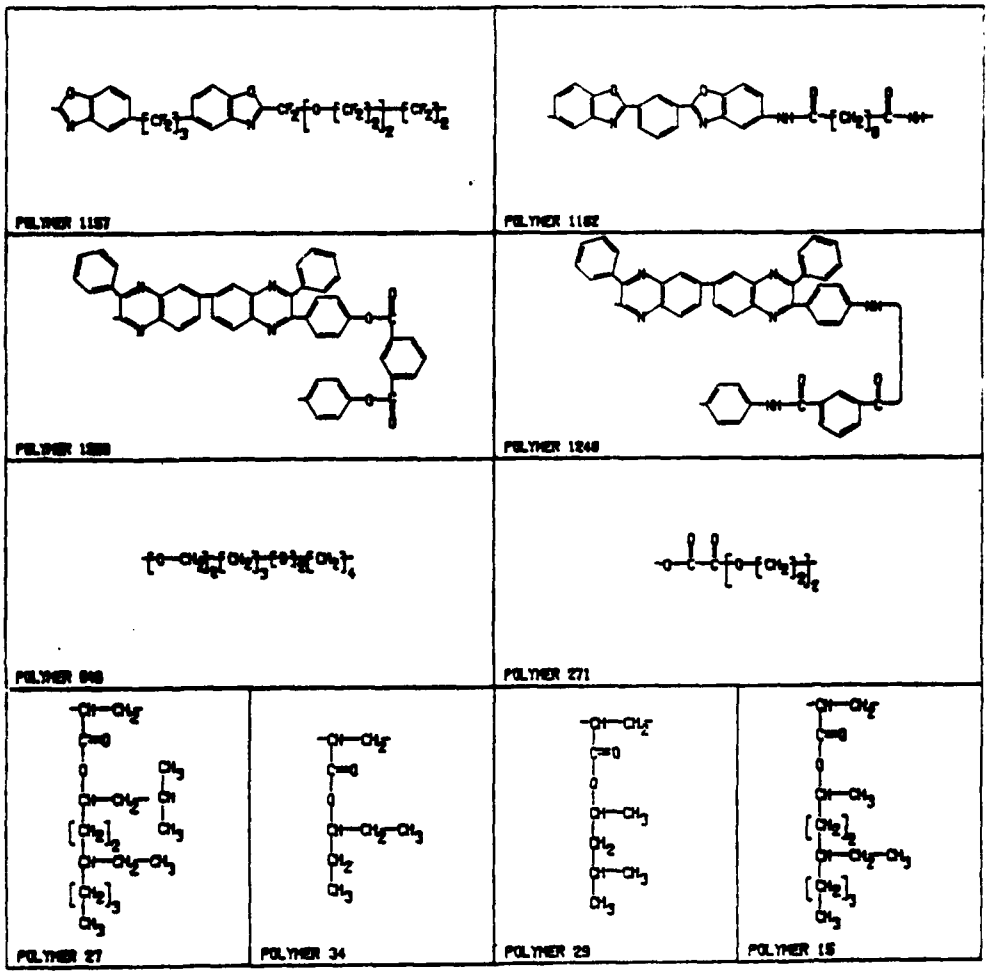
52	137	153	160	21	182 TRANS	27	32
157	180	20	158	471	470	469	468
467	466	465	464	463	462	461	460
459	458	457	456	455	454	453	452

Table 1 (Concluded)

133	131	15	130	200	371
 370	 369	 368	 367	366	365
 364	 363	 362	 361	360	359
 358	 357	 356	355	354	353
352	7	128	178	79	
98	95	96	177	75	 74
73	218	125	124	127	111
30	107	24	174	61	62
ISOTACTIC 46	45	36	44	25	1

Table 2

ILLUSTRATIONS OF SENIORITY CRITERIA



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No.	Author	Title, etc
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2	W.A. Lee	A hierachical system for the classification of single-stra organic polymers. RAE Technical Report 75105 (1975)
3	-	International Union of Pure and Applied Chemistry (IUPAC) Macromolecular Division Tentative Nomenclature of Regular Single-Strand Organic Polymers. J. Polymer Sci., Polymer Letters Edition, II, 389-414 (1972
4	A.M. Pattersen L.T. Capell D.F. Walker	The Ring Index. 2nd Edition. American Chemical Society, Washington, 1960

REPORT DOCUMENTATION PAGE

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Part I Rules for hierarchical ordering of the data set

7a. (For Translations) Title in Foreign Language

7b. (For Conference Papers) Title, Place and Date of Conference

8. Author 1. Surname, Initials	9a. Author 2	9b. Authors 3, 4	10. Date	Pages	Refs
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16. Descriptors (Keywords) (Descriptors marked * are selected from TEST)
Glass transition. Polymers. Classification. Hierarchy. Rules.

17. Abstract

The rational ordering of polymers in a large data set for the correlation of glass transition temperature (Tg) with structure requires the establishment of seniority criteria. An extension of polymer nomenclature rules published by the International Union of Pure and Applied Chemistry is proposed and applied, with examples, to the groups in a large polymer data set. The rules can be extended to cover new polymers without upsetting the original order.

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